1920
C431

H. M. Chiles

# Nitrogen in the Coking Process

# NITROGEN IN THE COKING PROCESS

BY

HOWARD MARION CHILES
B. S. University of Illinois, 1917

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## THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1920

1920
C43i

# UNIVERSITY OF ILLINOIS

## THE GRADUATE SCHOOL

May 31st 19120

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY HOWARD MARION CHILES

ENTITLED NITROGEN IN THE COKING PROCESS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

S. W. Parr
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in*

| | |
|---|---|
| ______________________ | Committee |
| ______________________ | on |
| ______________________ | Final Examination* |

*Required for doctor's degree but not for master's

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# ACKNOWLEDGMENT

The writer wishes to express his thanks to Professor S. W. Parr for his kind suggestions during the course of this work. The problem was suggested by him and was carried out under his supervision.

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TABLE OF CONTENTS

| | | Page |
|---|---|---|
| I | INTRODUCTION | 1 |
| II | HISTORICAL | 7 |
| III | EXPERIMENTAL | 13 |
| IV | SUMMARY AND CONCLUSIONS | 36 |
| | BIBLIOGRAPHY | 40 |

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# NITROGEN IN THE COKING PROCESS

## I INTRODUCTION

Although nitrogen is one of the most abundant of elements, the known sources of fixed nitrogen are rapidly reaching the point where the supply will no longer meet the demand. This is most fully realized if we accept the statement that the known deposits of Chili saltpeter will be exhausted in comparatively few years at the present rate of consumption.

This element in the fixed form is of the most supreme importance, both in the chemical industries and in the metabolism of plants and animals. Our vital needs for fixed nitrogen are constantly and rapidly increasing, due to the depletion of our soils and the constantly increasing uses in the chemical industries.

These reasons explain the interest which has been taken in the past few years in any means which will increase our available supplies of this important element.

The most important sources of nitrogen in the fixed form are as follows: Chili saltpeter, the atmosphere by combining with other elements under the influence of heat, electricity or the action of certain bacteria, and from the destructive distillation of coal.

The end of the supply of nitrogen from Chili saltpeter, as has been pointed out repeatedly, is in sight, and further, the cost of production from this source will increase more and more as the supply nears exhaustion.

Although several processes have been introduced in the past few years for the fixation of atmospheric nitrogen, it is not believed that these processes can compete in normal times with processes where the fixed nitrogen is obtained as a by-product.

The fixation of nitrogen by bacteria, although quite important, is of limited application due to the fact that no economical means for so fixing nitrogen has been devised, aside from the action of these bacteria while on the roots of certain leguminous plants.

The recovery of nitrogen as ammonia, from the products of destructive distillation of coal may be accomplished quite completely and economically. However, the yield of ammonia from a given coal varies greatly according to the method by which the coal is treated.

When coal is treated for the manufacture of Mond gas, yields as high as 85-90% of the total nitrogen of the coal can be recovered as ammonia. If all our coal could be treated in this way, little more could be expected in the way of nitrogen recovery. However, for economical and practical reasons it has not been possible to treat more than a very small amount of the coal used in this way.

In the ordinary coking processes, only a small part, usually from 10-15% of the total nitrogen of the coal, is obtained as ammonia. While a larger percentage, from 15-50% of the total nitrogen, is lost as free nitrogen in the gas, another small percentage, usually amounting to from 1-2% of the total nitrogen, is present

as cyanogen in the gas; and another small percentage of the nitrogen is obtained as organic nitrogen compounds in the tar. The remainder of the nitrogen, usually amounting to from 30-65% of the total nitrogen is retained in the coke.

Very little is known concerning the exact manner in which this nitrogen is held by the coke, but whatever the nature of the combination, the nitrogen is held in such a way that it is not displaced by heat along at temperatures, say of 1000° C, such as exist in the coking process.

Various assumptions have been made as to the nature of the combination without any real proof being known. It has been quite generally assumed by many (21) that the nitrogen was present as some very stable carbon, hydrogen and nitrogen compounds which were originally present in the coal, or as degredation products of the same. Others, have assumed that the nitrogen was held as adsorbed nitrogen on the surface of the carbon, but there exists quite a difference of opinion as to the real nature of adsorption processes. Still others (28) have assumed that the nitrogen is held as carbon nitride.

The assumption that the nitrogen is held as a very stable organic compound originally present in the coal or as degradation products of such compounds, appears untenable in view of the fact that the nitrogen is retained by the coke at temperatures at which all known compounds of similar type are completely decomposed. However, until we have a more complete knowledge of the composition of coal, as well as of coke, the statement cannot well be disproved.

The contention that the nitrogen is adsorbed on the surface of the carbon has a different aspect according to what view is taken as to the nature of the adsorption processes. Views on the nature of adsorption processes varyfrom the clear logical conception of Langmuir (27), others who view the process as strictly a physical phenomena, and the views of others which are expressed in terms of various mystic forces about which we know nothing. If we accept the view that the nitrogen is held by purely physical forces, it should be displaced by other gases of higher viscosity. This appears not to be the case, unless these substances are decomposed at the temperature used. If we consider the views of Langmuir, the ideas would not appear to differ fundamentally from those who consider that the nitrogen is retained as carbon nitride.

The assumption that the nitrogen is held as carbon nitride would account for the stability of the compounds toward heat, and the fact that they can be decomposed by hydrogen (21) and still more readily by steam and other substances which liberate hydrogen in the nacent state. By either of these methods the nitrogen is liberated as ammonia, not as free nitrogen (31). However, if we accept the formation of nitrides in the usual sense, we would have to assume such compounds of an unreasonably high percentage of carbon.

The purpose of this investigation was to obtain a better idea of the nature of the combination of the nitrogen with carbon. A working theory was formulated to account for the facts brought out in the foregoing discussion and also conforming to the principles

of a theory proposed by Langmuir for similar compounds.

If we consider a particle of pure carbon, the valences of the carbon atoms on the interior of the particle may be considered to be completely saturated by combination with the adjacent carbon atoms. The surface layer of carbon atoms, however, should be unsaturated and probably these surface atoms are held together in the manner of our ordinary conception of multiple unions. Consequently the surface layer of atoms should be quite reactive and combine with other elements much more freely than carbon atoms whose valences are completely saturated as in the interior of the carbon particle.

The nature of the elements which may add to these unsaturated valences most readily, however, may vary from that in common organic unsaturated compounds, due to the influence of the other elements in the molecule of the latter compounds. Also, the combination of one element with the carbon would probably produce a compound with which other elements would combine with more or less readiness than in the case of pure carbon. Further, as is well known, elements in the nacent or atomic state add much more readily to multiple unions than the same elements in the molecular state, particularly in the case of such stable molecules as nitrogen.

In the coking process, we have the decomposition of the compounds of the original coal with the production of carbon and the further decomposition in contact with the carbon of hydrocarbons, nitrogen compounds, sulphur compounds, etc., probably, with the production of elementary hydrogen, nitrogen, sulphur, etc. We might assume, therefore, that the original surface unsaturation of the

carbon particles would become saturated with these elements produced in the atomic state in contact with the carbon. Further, the amounts of each of these elements so held would depend upon several factors, namely, the specific reactivity of each of these elements with carbon and the stability of the compounds so formed, the relative proportions of the respective elements produced in contact with the carbon and also the previous combination of one or more of these elements would produce a surface with which the other elements would react with more or less readiness than in the case of the original carbon surface.

## II HISTORICAL

It has long been known that a large part of the nitrogen in coal is retained by the coke after the completion of the coking process. As the value of ammonia became more and more evident, it would be surprising indeed if serious efforts were not made to recover this nitrogen in the fixed form. In fact the literature, particularly the patent literature, has for a number of years carried numerous proposals for the recovery of this nitrogen.

In spite of the number of proposals for the recovery of this nitrogen from the coke, there appears to have been few serious attempts made to determine the exact nature of the combination between the nitrogen and the coke.

Swindell (1) in 1843, proposed to form ammonia by passing a mixture of nitrogen or nitrogen oxides and steam over red hot coke in a closed retort. It is probable that he never synthesized any ammonia from the nitrogen passed over the coke, particularly in the case of the free nitrogen. He, as well as many other of the early workers, probably obtained their ammonia from the nitrogen compounds in the coke and presumed it was formed from the atmospheric nitrogen.

Further patents were taken out by Binks, Armengared and Ertel (2) along the same line. Berthelot (3) in 1868, combined acetylene and nitrogen to form HCN under the influence of the electric spark.

Langlois (4) obtained ammonium cyanide by passing ammonia over hot charcoal and called attention to the remarkable way with which

ammonium cyanide resisted decomposition at high temperatures. Lewes disproves this early idea of Langlois, Kuhlmann and others that ammonium cyanide is formed and is stable at high temperatures, and that is the reason that the ammonia is not completely decomposed, by saying that both hydrogen sulphide and carbon dioxide "can turn it out of combination". This is undoubtedly true in the case of solutions, but he cites no evidence for the effect in gaseous form at high temperatures.

Ireland and Sugden (5) pass air and steam over heated peat coke or coal at a temperature not over 500° C. In this case they claim that the carbon burns slowly, hydrogen is formed which combines with the nitrogen of the air and forms ammonia. It is quite likely that their ammonia came from the coke.

Hennin (6) states that the formation of ammonia in coking takes place principally at a temperature of above 1000° and that below a red heat the formation of ammonia ceases, which proves it to be a secondary product. Later work, however, appears to show that the ammonia obtained in coking also comes from primary decomposition. He also stated that the hydrogen necessary for the formation of ammonia comes from the "constitution water" as verified by the fact that only 10% of the nitrogen in coal is transformed into ammonia in a gas retort, while 15% is obtained in a blast furnace with steam blast.

Simmersbach (7) gives some data on the formation of ammonia during carbonization of coal in an electrically heated tube.

Knublauch (8) states that the yield of ammonia from "seischlick" is greatly increased by mixing with coal before

distillation.

A. T. Smith (11) mixes leather with coal or coke and lime and treats in a gas producer, obtaining 70% of the nitrogen in the leather as ammonia.

F. Schreiber (9) investigated the catalytical production of ammonia from nitrogen carbon compounds by heating with carbon and iron oxide to 350° C and obtained from 47-73% of the total nitrogen as ammonia.

Heckert (10) employs for the same purpose the red hot coke from gas retorts.

Woltereck (12) claims to have obtained ammonia by bubbling air through water heated to 80° C and passing over carbon heated to not over 700° C.

Frank and Caro (13), however, disputed his claim that he produced ammonia from atmospheric nitrigen, claiming the ammonia came from the nitrogen compounds in the carbon used.

Woltereck (14) published results of another set of experiments in which he claimed to produce ammonia equal to 1% of the carbon consumed by passing steam and air over sugar carbon.

Peacock (15) produces ammonia by burning sulphur with a limited supply of air, to deprive the air of nearly all its oxygen and bringing the resulting mixture of $SO_2$ and $N_2$ into contact with carbon at about 800° C, claiming to form the compound $S_3N_4(C_3H_4)_2$ or $S_3N_4(C_3H_4)_3$ and treating the resulting product with hot water or steam to produce ammonia.

Berthelot (16) states that pure carbon free from hydrogen

and all traces of alkalis and alkaline earths does not combine with nitrogen to form cyanogen under the influence of heat at any known temperature.

M. Mayer and V. Altmayer (17) have investigated the influence of temperature on the formation of ammonia in the destructive distillation of coal. They find that the quantity of ammonia which a coal will yield at a given temperature depends upon the composition of the coal. The presence of $CO_2$ and CO promotes the liberation of nitrogen from coal at high temperatures, but the ammonia liberated in the first instance is to a great extent decomposed. This decomposing effect is promoted by the presence of iron or its compounds, consequently a high percentage of ash may be injurious to the yield of ammonia.

Simmersbach (18) found that the temperature of formation varies with different coals from 800 to 900° C. Decomposition of ammonia during gasification begins at 800° C and increases with rising temperatures. The quantity of cyanogen formed amounts to 1.5% of the total nitrogen and to 5% of the ammonia. Water lowers the yield of cyanogen and raises that of ammonia, while high gas velocities favors the formation of cyanogen. The size of the grain of coal has no effect on the yield of ammonia.

The same author in a later paper (19) summarizes his eariler results and added that the formation of cyanogen increases with the quantity of ammonia and with a rise in temperature.

E. Schilling (20) studied the effects of liming on coal during carbonization and found that it had a widely varying effect on different coals. He entirely disproved the statement of Guegnen

and Parent that the increase in ammonia yield by liming was due to the water of hydration of the lime furnishing additional steam in the retort, and that the contrary was decidedly the case.

Schilling also believed that coals which contain little oxygen give more of their nitrogen as ammonia than coals high in oxygen. However, this observation did not hold in all cases.

In the same paper, Schilling shows that most of the previous estimations of nitrogen in coal, according to the method of Duma or with soda lime, are inaccurate. He used the Kjeldahl method.

Tervet (22) obtained considerable increase in ammonia yield by passing hydrogen over the coke in retort at high temperatures. He also tried the effect of other gases upon the ammonia yield, and found that methane, carbon dioxide and nitrogen had no effect and that carbon monoxide had but very little.

W. Foster (23) tried the effect of large excess of steam upon coke, using 16 times the theoretical amount of steam. He obtained 61.6% of the nitrogen in the coke as ammonia, 35% remaining in the coke and 3.4% unaccounted for.

H. Techaner (24) states that when coke is treated with steam at 800 to 900° C, as much as 85% of the total nitrogen can be obtained as ammonia.

L. Weisberg (25) studied the decomposition of ammonia by carbon with production of HCN and found that the reaction was very slow with graphite. In fact, he was not certain that any HCN was formed. With sugar carbon, at a temperature of about 800° C, approximately 50% of the ammonia was transformed.

Weisberg concludes from his observations that the dissociation of ammonia, although a slow reaction, takes place faster than the decomposition of HCN, but slower than the formation of HCN.

Haber (26) has thoroughly investigated the formation of ammonia from the elements and calculated the dissociation constant as well as determined the effects of various catalysts upon the spped of formation.

Langmuir (27) has developed a theory for surface adsorption, in which he advanced the idea that adsorption on surfaces are often held in a similar manner to true chemical compounds.

# III EXPERIMENTAL

It was realized at the outset that a knowledge of the nature of the nitrogen compounds in coal would be of great value in determining the nature of the residual nitrogen compounds left after the coking process.

For the purpose of a better insight into the nature of these compounds, a few simple experiments were tried upon a sample of an air-dried coal (Sample No. 83).

One hundred grams of this coal were weighed out and refluxed for 12 hours with 250 cc.of 20% HCl, the acid was filtered off and the residue washed and the combined acid filtrate and washings were concentrated under partial vacuum at a temperature of 35-40° C. The resulting concentrated solution was made up to a volume of 50 cc. with water, and 5 cc. portions were treated by the Van Slyke nitrous acid method for the determination of amino nitrogen, in a micro Van Slyke machine. The volume of nitrogen obtained was scarcely measurable even after shaking for 2 hours at a temperature of 25° C. This showed that if the nitrogen in the coal was a residue from plant or animal proteins, the nature of the nitrogen compounds has greatly changed from that of the original nitrogen compounds.

Ten grams of the same coal was heated with 35 cc. of acetic anhydride on the water bath for a period of 8 hours, in a flask provided with a reflux condenser. When this solution was vigorously boiled, the vapors gave a red coloration to a pine splinter moistened with concentrated HCl, a test given by Mullikin (32) as characteristic of pyrrole and pyroll derivatives. This solution

when treated with an aquous solution of sodium nitrite gave an intense red coloration quite similar to that given by a small amount of pyrrol.

One hundred grams of the same coal, ground to pass a 100-mesh sieve, was treated with 250 cc. of 50% acetic acid and 20 grams of zinc added in small portions from time to time, while the flask was gently warmed on a water bath. The reaction was continued for 10 hours, and the resulting solution was made distinctly alkaline by the addition of 50% NaOH solution, and the solution extracted three times with 200 cc. portions of ether. This ether extract was concentrated to a volume of 100 cc. by distilling from a water bath heated to 50° C. The concentrated ether extract was then dired over $CaCl_2$ for 24 hours and the solution was then treated with dry HCl gas at 0° C. A small amount of a fine white crystalline precipitate was at first formed, but upon the addition of more HCl gas the precipitate disappeared.

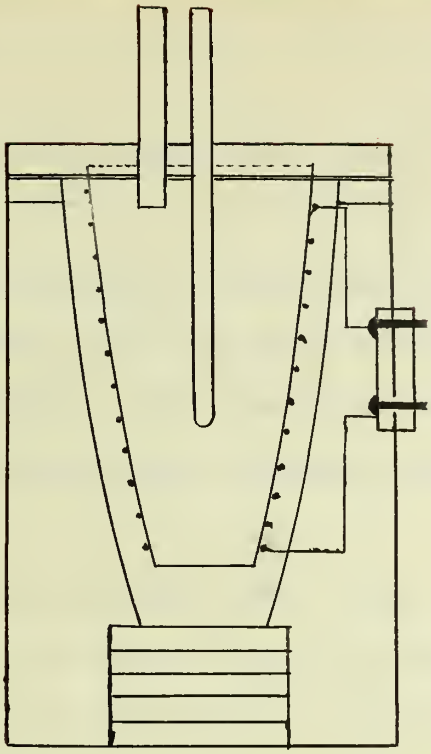
Now, if pyrrol or its derivatives were present in coal, we might expect them upon reduction to become more basic and consequently to form fairly stable hydrochlorides, which appears to be the case upon the first addition of HCl gas. However, as is well known, this treatment with HCl gas also causes pyrrol to polymerize and possibly this may be an explanation for the disappearance of the precipitate first formed.

The coal residue from this reduction was washed thoroughly with 95% alcohol, the first washings passing through with a white turbidity. The later washings were red in color and quite clear.

When these red alcoholic washings were diluted with water, however, the red coloration disappeared and the solution showed again the white turbidity and a slight yellowish precipitate formed, which upon standing changed to a reddish-brown colored resinous mass. A sodium fusion on this mass showed nitrogen to be present. The alcoholic solution upon dilution had a slight but very nauseous odor, such as one might expect to result from a mixture of linseed oil varnish with a small amount of ethyl isocyanate.

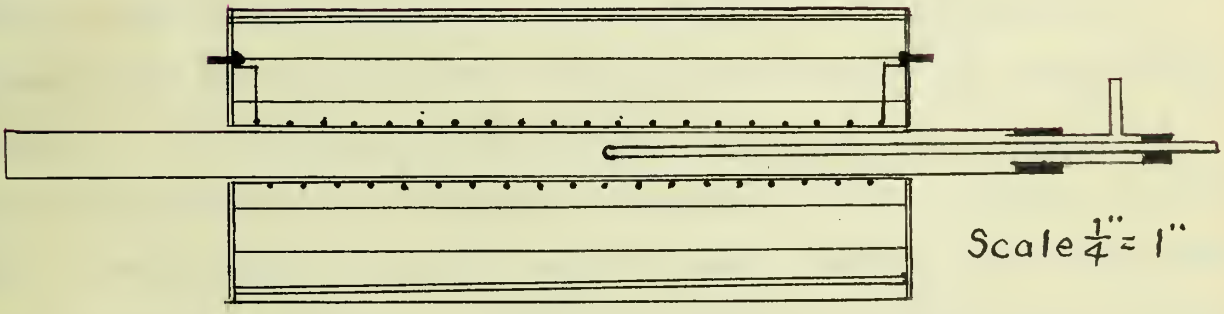
Any assumption that coal contains pyrrol derivatives would be borne out by the work of Pictet (29) who by the vacuum distillation of coal was able to isolate from the products nitrogen compounds of the following empirical formulas: $C_8H_7N$, $C_9H_9N$, $C_{10}H_{11}N$ and $C_{11}H_{13}N$ and $C_{12}H_{15}N$. These products were stated by him to be secondary amines. Compounds of any of the above formulas might be assumed to be formed by condensing a pyrrol ring with benzene or its homologues that are known to be a product of the distillation of coal.

One would expect upon distillation that such compounds would decompose mainly in such a way as to destroy the pyrrol ring owing to the greater stability of the benzene ring. Further, the presence of pyridine and quinone in the distillation products would be accounted for because Pictet (30) and his co-workers have formed pyridine by the distillation of methyl pyrrol through a heated tube. Indeed, it should not be surprising to find pyrrol derivatives in coal if we assume the vegetable origin of coal, due to the preponderance of pyrrol rings in the molecule of chlorophyll (14) and other plant coloring matters. Pyrrol and indol rings are also



Scale $\frac{3}{8}$" = 1"

Fig. I



Scale $\frac{1}{4}$" = 1"

Fig. 2

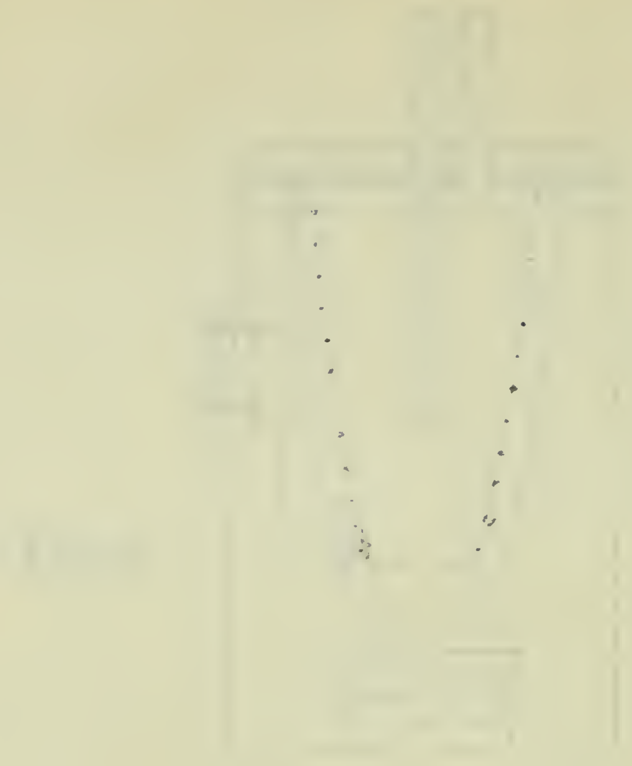
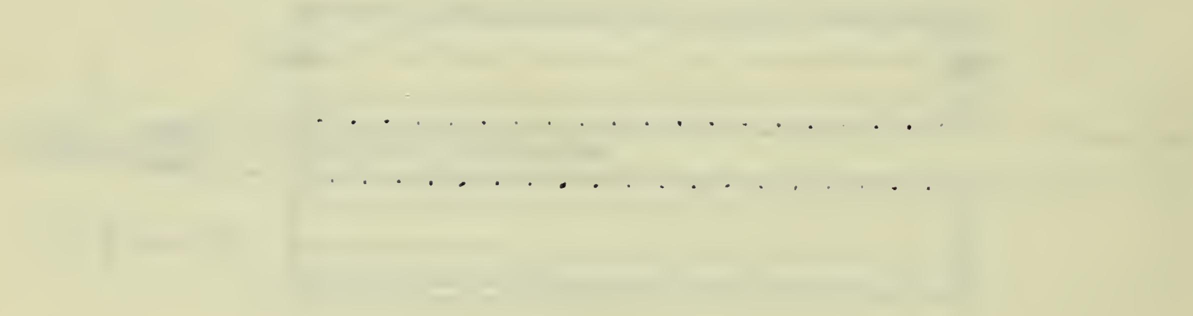


Fig 3



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present in several of the constituent amino acids of both plant and animal proteins.

Due to the small amount of materials obtained by these various treatments and the lack of time, work with the nitrogen compounds in coal was discontinued. The remainder of the time was spent in the production and study of the nitrogen compounds in coke and other forms of carbon.

For this purpose petroleum coke, coke, wood charcoal and sugar carbon were used for the carbon material, and the following substances were used to furnish the nitrogen: egg albumen, casein, diphenyl sulfourea, diphenyl piperazine, sodium cyanide, ammonia and cyanogen.

The last two named materials were passed over the carbon heated in a small resistance electric furnace, while in the case of the other solid materials, weighed amounts were mixed with the carbon and the mixture heated in the electric furnace.

The temperature of the furnace was determined in all cases by means of a Pt-Rd thermocouple enclosed in a fused silica (vitreosil) tube. The tube bearing the thermocouple in every case was so placed that the junction was located in the center of the heating chamber. The heating of the furnace was regulated by means of carbonblock rheostats connected in series with the furnace. In this way it was found to be quite easy to keep a sufficiently close control of the temperature. The fluctuations in temperature throughout a run never varied over 10° C from the recorded temperature.

The runs numbered from 1 to 18 inclusive were made in a small pot type electric furnace (Figure 1). This furnace was construct-

ed by winding No. 22 Nichrome wire in a helical groove ground on the outside surface of a No. 20 fire clay assaying crucible. The winding was then covered with a paste made from alundum cement and water and while this covering cement was still wet, this heating element was fitted inside another larger fireclay crucible. This second crucible had holes drilled through the walls to accomodate the lead-in wires for the heating coils. The alundum cement was then dried in a drying oven and finally by passing a small electric current through the heating coils. This heating element was then placed inside an iron can and the remaining space filled with "Sil O Cel". The bottom of the crucible containing the heating element rested on a support made from several pieces of asbestos board and the top was supported by a layer of dried paste of alundum cement and asbestos pulp. The cover for the furnace was made by taking the original cover for the can and filling with a paste of asbestos pulp and alundum cement. A porcelain tube was provided for the purpose of leading off the gases formed, and a fused silica tube for the thermocouple. The cover fitted quite snugly, but in use the joint between the cover and the furnace was luted with a paste of fireclay and water glass.

The runs numbered from 200-236 inclusive were made in a combustion type electric furnace (Figure II). This furnace was made by winding No. 18 Nichrome wire in a groove ground on the surface of a heavy alundum tube. After winding the wire, the windings were covered with a heavy layer of alundum cement and after this was dry the heating element was insulated with two layers of "85% magensia"

steam pipe insulation material. The ends of the furnace were finished by circular pieces cut from heavy transite board and held in place by two iron rods extending the length of the furnace.

The materials to be heated in this furnace were placed in a fused silica combustion tube which fitted closely inside the alundum tube of the heating element. In runs employing five grams or less material, the carbon was placed in a large porcelain combustion boat. When larger amounts of material were used, it was placed directly in the silica tube.

All nitrogen determinations on coals and cokes were made by the Gunning-Kjeldahl method, using N/10 solutions of sulphuric acid and sodium hydroxide for the titrations with methyl red as indicator.

The ammonia present in the gases evolved was absorbed by passing the gases successively through three Drexel wash bottles half filled with 5% sulphuric acid. The ammonia present in this wash liquid was determined by neutralizing with 35% NaOH solution and distilling into N/10 sulphuric acid as in a Kjeldahl determination.

For the purpose of testing the constancy of the content of nitrogen introduced into carbon by various nitrogen compounds, samples of petroleum coke were heated with various nitrogen compounds and the nitrogen in the coke determined (Table I). At the conclusion of each run, the furnace was swept out with a stream of dry nitrogen gas for thirty minutes.

In Run No. 15 (Table I), after heating for the usual two hours, the petroleum coke was cooled and washed with hot water until the wash water gave no precipitate with a solution of $AgNO_3$. The coke

## TABLE I

Nitrogen Introduced into Petroleum Coke by Various Materials

| Sample No. | Expt. No. | Wt. Gms. | Temp. °C | %N in C After Treatment | %N in C Before Treatment | Nitrogenous Material Added |
|---|---|---|---|---|---|---|
| 1 | 6 | 25.0 | 800 | 1.11 | 0.886 | 2.5 gms. Egg Albumen |
| 2 | 7 | 25.0 | 800 | 1.14 | 0.886 | 5.0 gms. Egg Albumen |
| 3 | 10 | 25.0 | 800 | 1.00 | 0.886 | 0.5 gms. Egg Albumen |
| 4 | 201 | 4.0 | 850 | 1.20 | 0.886 | $NH_3$ |
| 5 | 202 | 4.0 | 850 | 1.02 | 0.886 | $NH_3$ |
| 6 | 204 | 4.0 | 850 | 1.18 | 0.886 | $NH_3$ |
| 7 | 13 | 4.0 | 850 | 1.13 | 0.886 | 2.5 grams of Casein |
| 8 | 11 | 25.0 | 850 | 0.97 | 0.886 | 2.5 gms Diphenyl Piperazine |
| 9 | 12 | 25.0 | 850 | 0.93 | 0.886 | 2.5 gms Diphenyl Sulfourea |
| 10 | 15 | 25.0 | 850 | 0.31 | 0.886 | 2.5 grams of NaCN |

Time for each run was 2 hours

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was then dried for 8 hours at a temperature of 110° C. Samples were then weighed out and analyzed for nitrogen.

The results of these tests seem to show that there is a constant percentage of nitrogen which is retained by the coke when treated with an excess of ammonia or albuminous matter which is known to yield ammonia upon destructive distillation. However, when the same coke is treated with other nitrogenous materials of such a character that they may not yield ammonia upon distillation, there is only a slight increase in the nitrogen content.

The treatment with NaCN shows quite a decrease in the nitrogen content of the coke, which is not surprising when we consider the alkaline character of NaCN and also its formation in the presence of an excess of carbon in several methods for the fixation of nitrogen.

It was thought advisable next to carry out a somewhat similar set of runs using coke from coal, as it was thought possible that the ash constituents of the coke might influence the retention of nitrogen. In order to have coke of known origin, as well as to study the behavior of the particular coal at hand, a few coking experiments (Table II) were carried out.

These experiments were carried out in an electrically heated iron pipe furnace. The coke obtained from each of these runs was hard and of good quality and was used for a number of other experiments.

The results of these coking experiments show good agreement with the average results obtained in large scale practice as well

as that of other published laboratory experiments.

TABLE II

Coking Experiments on Coal

| | | | | | |
|---|---|---|---|---|---|
| Sample No. | 82 | 83 | 83 | 83 | 83 |
| Run No. | 101 | 102 | 103 | 104 | 105 |
| Wt. Sample Grams | 200 | 300 | 300 | 300 | 250 |
| Temp. ° C | 800 | 800 | 800 | 850 | 850 |
| % N in Coke | 1.35 | 1.19 | 0.95 | 1.13 | 0.62 |
| % S in Coke | 1.97 | 3.17 | 2.48 | 3.36 | |
| % N in Coal | 1.41 | 1.20 | 1.20 | 1.20 | 1.20 |
| Wt. Coke Grams | 120 | 176 | 168 | 167 | 135 |
| Wt. N in Wash Acid, gms. | 0.454 | 0.606 | 1.376 | 0.682 | 0.925 |
| % Tot. N Recovered as $NH_3$ | 16.11 | 16.82 | 38.21 | 18.92 | 30.8 |
| % Tot. N in Coke | 57.5 | 58.3 | 43.3 | 52.4 | 33.5 |
| Time, hours | 2 | 2 | 1-3/4 | 2 | 2 |
| Conditions | | | Last 3/4 hr. with steam | | Steam |

The nitrogen eliminated from the coal is in every case considerably higher than the nitrogen recovered as ammonia, showing the probability that a part of the nitrogen is distilled as other nitrogen bases as well as the destruction of a part of the ammonia formed. The work of Ramsey and Young (33) showed that ammonia may be completely decomposed at a temperature of 780°. There is

less destruction of the ammonia shown in the tests carried out with steam which is also in accordance with the observations of others.

These tests with steam show a much higher elimination of nitrogen from the coke. This result is to be expected if we assume a concentration of the nitrogen on the coke surface, while if the nitrogen is evenly distributed throughout the coke mass, we would expect the same percentage of nitrogen in the coke after a 3/4 hour treatment with steam as with a longer treatment.

Other experiments (Table III) were carried out in the same manner as those shown in Table I, with the object of testing the constancy of the nitrogen content of different forms of carbon after treatment with various nitrogenous substances.

It will be noted that the percentage of nitrogen retained by coke samples when treated with ammonia or othernitrogenous materials is quite comparable to that retained by petroleum coke when treated with the same materials. The nitrogen retained by wood charcoal is interesting due to the low value. If we were to assume the nitrogen to be held by simple capillary forces, we would expect the nitrogen held by wood charcoal to be quite large in comparison with that retained by coke due to the greater porosity ofthe charcoal.

It was realized in the preceding experiments that the ash and other foreign constituents in the coke and petroleum coke might influence the amount of nitrogen retained. For this reason, sugar carbon was used for a set of experiments to determine the amount of nitrogen retained by such carbon when treated with

## TABLE III

## Nitrogen Introduced into Different Forms of Carbon

| Sample | Run No. | Wt. Gms. | Temp. °C | % N in Coke Residue | % of N in Original Coke | Material Used |
|---|---|---|---|---|---|---|
| Coke 104 | 200 | 5.00 | 750 | 1.41 | 1.13 | $NH_3$ |
| Coke 104 | 225 | 5.00 | 850 | 1.30 | 1.13 | $NH_3$ |
| Coke 103 | 229 | 5.00 | 850 | 1.00 | 0.95 | 2.5 grams of Casein |
| Wood Charcoal | 14 | 25.00 | 850 | 0.59 | 0.41 | 2.5 gms Egg Albumen |
| Coal 83 | 200 | 5.00 | 850 | 1.05 | 1.20 | $NH_3$ |
| Pet. Coke | 15 | 25.00 | 850 | 0.31 | 0.886 | *NaCN |
| Pet. Coke | 12 | 25.00 | 850 | 0.93 | 0.886 | 2.5 gms Diphenyl Sulfourea |
| Pet. Coke | 11 | 25.00 | 850 | 0.97 | 0.886 | 2.5 gms Diphenyl Piperazine |
| Sugar Carbon | 236 | 4.00 | 850 | 0.38 | 0.00 | $C_2N_2$ |
| Coke 105 | 22 | 10.00 | 850 | 0.66 | 0.62 | Diphenyl Sulfourea |

Time for each run was 2 hours

* In Run No. 15 above, after heating for the usual two hours, the sample was withdrawn and washed thoroughly with hot water on a Buchner funnel. After drying for eight hours at 110°, the total nitrogen in the sample was determined.

gaseous ammonia (Table IV).

TABLE IV

Nitrogen Introduced into Sugar Carbon by Ammonia

| Sample No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Run No. | 227 | 230 | 233 | 231 |
| Weight, gms. | 4.0 | 4.0 | 6.0 | 6.0 |
| Temp. ° C | 850 | 850 | 850 | 850 |
| %N in Residue | 4.92 | 6.0 | 4.48 | 4.89 |
| Atmosphere | $NH_3$ | $NH_3$ | $NH_3$ | $NH_3$ |
| Time, hours | 2 | 2 | 2 | 2 |

In all the above runs, expect Run No. 230, after heating for two hours with a stream of ammonia passing over the carbon, the ammonia stream was cut off and a stream of nitrogen passed through the furnace for 30 minutes. In Run No. 230, nitrogen was passed through the furnace at the conclusion of the run for only 10 minutes.

The results of the above runs using pure sugar carbon and ammonia show a much greater retnetion of nitrogen than in the case of the petroleum coke or coke previously used. It will also be noted that in the one case (Run No. 230) in which the furnace was imperfectly swept out, that the nitrogen content was noticeably increased. This suggested some further work to determine whether all of the nitrogen retained by carbon is held in the same way.

The high results for nitrogen retention obtained in these experiments led to the question as to whether the sulphur and

hydrogen content of coke influenced the amount of nitrogen retained, as was predicted might be the case in making the original assumption as to the nature of the process by which the nitrogen is held.

It was decided next to determine what effect, if any, the sulphur content of sugar carbon had upon the retention of nitrogen, and for sake of comparison corresponding experiments (Table V) were carried out using coke for the carbon material.

For this purpose the carbon was placed in two boats and a stream of dry $H_2S$ gas was passed through the heated furnace for two hours. The furnace was then swept out by passing a stream of dry nitrogen gas through it for thirty minutes. One of the boats was then removed and analyzed for sulphur. The other boat was left in the furnace and treated with dry ammonia gas for two hours, after which the furnace was again swept out with nitrogen for thirty minutes.

TABLE V

Retention of Nitrogen from Ammonia by Carbon Previously Treated with $H_2S$

| | Sugar Carbon | | | Coke No 104 | |
|---|---|---|---|---|---|
| Sample No. | 1 | 2 | 3 | 1 | 2 |
| Wt. Grams | 4.0 | 6.0 | 6.0 | 4.0 | 4.0 |
| Run No. | 228 | 232 | 235 | 224 | 226 |
| Temp. °C | 850 | 850 | 850 | 850 | 850 |
| %S in C After $H_2S$ | 2.36 | 2.42 | 2.47 | 2.84 | 2.96 |
| %N in C Before $H_2S$ | 0.00 | 0.00 | 0.00 | 0.96 | 0.91 |
| %N in C Before $NH_3$ | 2.13 | 2.78 | 2.23 | 1.27 | 1.14 |
| %N in C After $NH_3$ | 1.54 | 0.95 | 1.37 | 1.72 | 1.94 |

carbon not previously saturated with nitrogen, as it will be noted that the percentages of sulphur in the carbon while all quite high are not uniform for the different runs.

Probably these results may be explained on the basis of Langmuir's theory in that at least a part of this sulphur is held by secondary valences, while when sulphur is added previous to the addition of nitrogen, the sulphur is held by primary valences.

TABLE VI

The Effect of Nitrogen in the Carbon Upon the Retention of Sulfur

| | Sugar Carbon | | | |
|---|---|---|---|---|
| Sample No. | 1 | 2 | 3 | Coke No. 104 |
| Run No. | 227 | 233 | 234 | 225 |
| Wt. Grams | 4.0 | 4.0 | 6.0 | 4.0 |
| Temp. °C | 850 | 850 | 850 | 850 |
| %N in C Before $NH_3$ | 4.92 | 4.48 | 4.87 | 1.30 |
| %S in C After $NH_3$ | 0.00 | 0.00 | 0.00 | 2.19 |
| %N in C Before $H_2S$ | 3.29 | 2.94 | 3.02 | 1.05 |
| %S in C After $H_2S$ | 7.86 | 3.94 | 5.51 | 5.72 |

From the results of the last set of experiments, it seemed desirable to determine whether all the nitrogen held by carbon when treated with pure ammonia was held in the same way or whether a part of it at least might not be held in a more loose manner. For this purpose, samples were taken out during several of the runs after treating with ammonia for two hours, but before sweeping out

When the results of these experiments are compared with the results given in Table IV, it requires no comment to show that the previous addition of sulphur has a great influence upon the amount of nitrogen retained by the carbon when treated with ammonia. It will be noted, however, that the amount of sulphur retained by the coke is slightly higher than that retained by sugar carbon, while the amount of nitrogen which can subsequently be added to coke is very much less than that which can be added to sugar carbon. This suggests the possibility of the influence of the ash constituents of coke. Now, it is well known that by coking a mixture of coal and lime or other alkali, a large part of the nitrogen can be eliminated from coal. In view of this fact, it would not be surprising to find that the basic ash constituents would prevent the retention of nitrogen by the coke, at least to some extent.

A set of experiments (Table VI) was next performed to determine the effect of nitrogen in the coke upon the retention of sulphur. The experiments were carried out in exactly the same manner as in the previous experiments except that gaseous ammonia was passed through the furnace first for two hours and then after sweeping out the furnace with nitrogen,hydrogen sulphide was passed through the furnace for two hours.

The results of these experiments are even more remarkable than those in the previous ones. The increased retention of sulphur by carbon previously treated with ammonia was hardly to be expected. It is possible that the nature of the combination is of a different character from that existing in ordinary coke or

the furnace with nitrogen. These samples were analyzed (Table VII) for nitrogen and the remainder of the charge replaced in the furnace and nitrogen passed through the heated furnace for thirty minutes and the charge again analyzed for nitrogen.

TABLE VII

Nitrogen Held by Secondary Valences

| Sample | Pet. Coke | Sugar Carbon 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Run No. | 202 | 227 | 231 | 234 | 232 | 228 |
| Wt. Grams | 4.0 | 4.0 | 4.0 | 6.0 | 6.0 | 4.0 |
| Time, hours | 2 | 2 | 2 | 2 | 2 | 2 |
| Temp. °C | 850 | 850 | 850 | 850 | 850 | 850 |
| %N Before Sweeping | 1.51 | 6.60 | 6.68 | 6.64 | 2.98 | 3.21 |
| %N After Sweeping | 1.02 | 4.92 | 4.89 | 4.48 | 2.78 | 2.13 |

The results of these experiments seem to indicate that a part of the nitrogen is held in a less firm manner than the remainder, particularly in the case of the carbon not previously treated with sulphur. This is exactly the reverse of the indications in the case of sulphur. These results are in accord with the work of Langmuir, and in terms of his theory would be explained by saying that this more loosely held nitrogen is retained by secondary valences, while probably the remainder of the nitrogen is held by primary valences.

It was thought that the nitrogen held in this more loose manner might be obtained as ammonia by merely distilling with a

strong solution of sodium hydroxide. For the purpose of determining whether this was the case or not (Table VIII), portions of the samples withdrawn in the last set of experiments for the determination of total nitrogen were taken and distilled with 250 cc. of 5% sodium hydroxide as in a Kjeldahl determination, blank determinations using pure sugar carbon being run at the same time.

TABLE VIII

The Effect of Boiling Nitrogen Bearing Carbon with 5% NaOH

| Sample | Sug. C + N | Sug. C + S + N | Blank-Sug.C | Coke 101 |
|---|---|---|---|---|
| Wt. Gms. | .5000 | .5000 | .5000 | .5000 |
| Run No. | 233 | 232 | | 101 |
| Treatment | Boiled with 5% NaOH | Boiled with 5% NaOH | Boiled with 5% NaOH | Boiled with 5% NaOH |
| %N in C | 4.48 | 2.78 | 0.00 | 1.35 |
| Cc. of N/10 $H_2SO_4$ Required | 0.25 | 0.34 | 0.22 | 0.25 |

The results of these experiments show that very little if any nitrogen is eliminated from these nitrogen bearing carbons by boiling with alkali.

Table IX shows the results given by treatment of the various cokes and other nitrogen bearing carbon with steam. The experiments were carried out in exactly the same way as the treatment of the carbon with ammonia and hydrogen sulphide. The steam was produced by boiling distilled water in a 1000 cc.distilling flask and passing the vapors through a water trap before entering the furnace. The samples were placed near the back of the furnace,

so that the steam was preheated by passing through the heated tube for about eight inches before reaching the samples. The boiling was regulated so that approximately 250 grams of water passed through the tube in a period of two hours.

TABLE IX

Effect of Temperature on Nitrogen Elimination of Coke No. 102

| Sample No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Weight, Gms. | 4.0 | 10.0 | 4.0 | 4.0 | 4.0 |
| Temp. °C | 350 | 400 | 500 | 650 | 800 |
| Run No. | 208 | 205 | 209 | 206 | 207 |
| %N Before Steaming | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 |
| %S Before Steaming | 3.17 | 3.17 | 3.17 | 3.17 | 3.17 |
| %N After Steaming | 1.19 | 1.15 | 0.96 | 0.92 | 0.76 |
| %S After Steaming | 3.01 | 2.79 | 2.25 | 2.04 | 1.79 |
| Time, hours | 2 | 2 | 2 | 2 | 2 |

In Table X is shown the results of treating coke with steam at varying temperatures. The data of these experiments is in agreement with that given in Table II in showing that the nitrogen in the coke is not evenly distributed, but as the total weight of carbon decreases by the action of steam, the percentage of nitrogen in the remaining mass decreases. That some nitrogen remains after the action of steam may be due to the fact that all the carbon surface is not accessible to the steam and it probably is

due to some extent at least to the recombination of the ammonia liberated with fresh carbon surfaces.

TABLE X

Effect of Temperature on Nitrogen Elimination of Coke No. 103

| Sample No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Weight, Gms. | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Temp. °C | 350 | 510 | 550 | 650 | 750 | 850 | 1000 |
| %N Before Steaming | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 |
| %S Before Steaming | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| %N After Steaming | 0.95 | 0.94 | 0.90 | 0.79 | 0.75 | 0.64 | 0.57 |
| %S After Steaming | 2.00 | 2.23 | 1.96 | 1.90 | 1.71 | 1.62 | 1.54 |
| Run No. | 218 | 220 | 222 | 219 | 221 | 223 | 216 |
| Time, Hrs. | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| % Tot. N Rec.as $NH_3$ | 2.01 | 7.10 | 8.86 | 29.32 | 26.20 | 35.20 | 23.80 |
| Wt.Residue Grams | 9.84 | 9.27 | 9.50 | 8.97 | 8.11 | 6.94 | 3.21 |
| % Tot.Orig. N in Coke | 98.30 | 91.70 | 90.00 | 70.80 | 60.80 | 40.00 | 18.30 |

That the compounds are of the nature of nitrides is indicated by the fact that at temperatures at which the water gas reaction becomes operative, the nitrogen is displaced with the formationof ammonia. While these compounds are not displaced by either heat at even much higher temperatures than those employed here, nor by saturated gases of higher viscosity unless decomposed

at the temperatures used.

Experiments (Table XI) were carried out to determine the effects upon the ammonia yields and nitrogen elimination by passing various gases through the furnace.

TABLE XI

Effect of Nitrogen Elimination of Various Gases on Coke No. 105

| Sample No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Weight, Gms. | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Temp. °C | 600 | 600 | 650 | 650 | 650 | 850 |
| Run No. | 210 | 211 | 212 | 213 | 214 | 217 |
| % of N In Residue | 0.48 | 0.59 | 0.62 | 0.52 | 0.54 | 0.58 |
| % of S In Residue | 1.61 | 2.60 | 2.44 | 2.41 | 3.67 | Lost |
| % of N In Orig. Coke | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 | 0.62 |
| % of S In Orig. Coke | 3.58 | 3.58 | 3.58 | 3.58 | 3.58 | 3.58 |
| Atmosphere | Steam | $H_2$ | CO | CO | $CO_2$ | $CH_4$ |
| Gms. $NH_3$ Recovered | .0057 | .0005 | .00133 | .0021 | .0009 | .0008 |
| % Tot. N Recovered | 9.19 | 0.81 | 2.15 | 2.38 | 1.45 | 1.38 |

The results of these experiments confirm those of Tervet (22) for gases other than hydrogen, however, the temperature used here in the case of hydrogen is probably lower than that employed by him. It would appear that hydrogen as employed in this experiment is more effective for the removal of sulphur than for nitrogen, or perhaps it would be better to say that the sulphur is more

easily removed than nitrogen when both are combined with carbon. This is probably due to the relatively greater dissociation of the carbon-sulphur compounds compared to the carbon-nitrogen combination. The question might be raised as to why CO displaces a part of the nitrogen as ammonia. This could be explained if we assume that we have present in the coke carbon-hydrogen surface compounds from which CO might displace the hydrogen and this hydrogen then in the nacent state could decompose the corresponding amount of carbon-nitrogen compound with the liberation of ammonia. Carbon dioxide and methane do not displace nitrogen at least not to the same extent, because they are completely saturated compounds and consequently will not decompose the carbon-hydrogen compounds, and therefore, there would be no nacent hydrogen to decompose the nitrogen compounds. Steam, by this theory, then would be particularly effective because by the water gas reaction, it forms hydrogen and carbon monoxide which might itself form surface compounds and thus prevent an equivalent amount of hydrogen from forming such compounds, and make a larger part of the hydrogen effective for decomposing the nitrogen compounds. It would appear necessary to assume some dissociation of the carbon-nitrogen compounds and then by combination with the nacent hydrogen and the removal of the resulting ammonia in the gases, the equilibrium of the carbon-nitrogen compounds would be displaced. That these compounds are very slightly dissociated at the temperatures employed would be shown by the large excess of hydrogen necessary for decomposition; or, in other words, the very slow rate of decomposit-

ion.

In order to determine whether nitrogen added to carbon by ammonia was held in the same way as nitrogen from organic compounds in coal, samples of carbon-nitrogen materials obtained in several of the runs with ammonia were treated with steam and the amount of nitrogen displaced determined.

Table XII gives the results of these tests, together with some typical tests upon natural nitrogen bearing cokes.

TABLE XII

| Sample | Sugar C N | Sugar C N | Coke 103 | Coke 101 |
|---|---|---|---|---|
| Wt. Grams | 4.0 | 4.0 | 10.0 | 10.0 |
| Run No. | 230a | 227 | 223 | 235 |
| Temp. °C | 850 | 850 | 850 | 850 |
| % N Before Steaming | 6.0 | 4.92 | 0.95 | 1.35 |
| % N After Steaming | 3.62 | 2.76 | 0.64 | 0.828 |
| Time, hrs. | 2 | 2 | 2 | 2 |
| $\frac{\text{\% N Remaining in Coke}}{\text{\% N in Original Coke}}$ | .603 | .561 | .673 | .613 |

The ratio (Table 12) of $\frac{\text{\% nitrogen remaining in the coke}}{\text{\% nitrogen in original coke}}$ was chosen, because owing to the difference in the nature of the carbon in the two cases, it was thought that the sugar carbon would probably be destroyed more rapidly than the coke from coal. Consequently a ratio based upon the percent of the total nitrogen remaining in the coke would be misleading because of the great

difference in the amount of carbon left in the two cases. The values for these ratios in the cases cited appear to be sufficiently close to assume tentatively at least that the nature of the combination between the nitrogen and the carbon is the same, whether the source of the nitrogen is ammonia or organic compounds such as are found in coal.

## IV SUMMARY AND CONCLUSIONS

It may as well be noted before the formulation of any conclusions that no claim is made as to having proven the nature of the combination of nitrogen retained by the coke. It is, however, believed that the work has made the original assumption, the most probable, namely, that the nitrogen is retained as surface compounds which seem to be in the nature of carbon nitrides appear at least a feasible explanation for the observed facts.

The similarity of behavior when treated with steam, and the approximately equal amounts of nitrogen added to a given kind of carbon by ammonia and albuminous matter and that present in coke from nitrogenous materials in coal, all point to a similar combination. That the combination formed by treating pure carbon, such as sugar carbon, with ammonia is the same as that of the nitrogenous compounds originally present in coal does not appear plausible. From these facts, one would naturally be led to think that the nature of the nitrogen compounds in coke derived from coal are entirely different from those originally present in the coal.

When coke is treated with steam, the interior of the coke particles when viewed after crushing show no evidence of any change, consequently the constantly decreasing percentage of nitrogen retained when treated with steam for different periods of time would seem to point at least to a concentration of nitrogen on the surface. That there are surfaces on the interior of the coke which are not subjected to the action of steam until the surrounding coke is removed appears probable. Therefore, it is quite

natural to assume that the residual nitrogen retained is due to the retention by these surfaces inaccessible to the action of steam as well as to the recombination of liberated ammonia on fresh surfaces.

The data obtained upon the effect of sulphur already combined with the carbon upon the subsequent addition of nitrogen points very clearly to the chemical nature of the combination. If the process was one of mere surface condensation, it is difficult to see why materials of lower viscosity such as nitrogen from ammonia would replace one of higher viscosity such as sulphur from hydrogen sulphide. The data also shows quite clearly that the process is a reversible one, as the nitrogen from ammonia can be replaced in turn by sulphur from hydrogen sulphide, though of course this displacement might be due to the action of the hydrogen also liberated. However, carbon monoxide, a substance of low viscosity appears to displace more of the nitrogen than carbon dioxide, a substance of higher viscosity.

That increased amounts of sulphur are retained by carbon previously treated with ammonia might appear to contradict the original assumption, but it would appear from the varying amounts of sulphur so retained that the combination was of a less firm nature. This is in accordance with the views of Langmuir, who recognizes two types of combination, namely: combination through primary valences and combination through secondary valences. The retention of sulphur upon a surface previously treated with ammonia would appear then to belong to this second type of combination, or

possibly the increased addition of sulphur can be explained by the effect produced when substances already added as in our ordinary organic addition products, have the property of extension by still further additions.

The facts observed by others upon the formation of cyanogen by treatment of carbon with ammonia might naturally be considered as the result of the formation of these carbon-nitrogen surface compounds. If we have present an excess of ammonia and assume dissociation of these carbon-nitrogen surface compounds, we would naturally expect that the excess of nitrogen would displace the equilibrium in such a way as to produce cyanogen, and this upon liberation would escape with the gases and further aid in displacing the equilibrium, so that we would have a ready explanation for the formation of cyanogen in the coking process, and the relations which have been observed by others (18) between the amounts of ammonia and cyanogen formed during the coking process.

The work so far accomplished is incomplete. In order to get a sufficient understanding of the problem it would appear necessary to obtain more information concerning the nitrogen compounds in coal. Valuable information might be obtained by studying the dissociation of the various compounds which may be present in coke. Further, light might be shed upon the question as to whether or not compounds are formed only on the surface by determining the amount of nitrogen retained by carbon in various states of mechanical division. With regard to the effects if any of the ash constituents, it would appear necessary to carry out a set of

nitrogen addition experiments with varying but known amounts and varieties of these ash constituents. Valuable information might be obtained concerning the nature of the combination by treating the nitrogen bearing cokes with acids and alkalies at higher temperatures under pressure. Further study might be made by treating the nitrogen bearing cokes with vapors other than water, which decompose with the formation of hydrogen. A careful study of the composition and pressure exerted by gases after treatment of carbon with ammonia might be valuable in determining the extent to which hydrogen enters into the addition product. A study of the effect of the addition of sulphur might well be further studied by using pure sulphur vapor rather than hydrogen sulphide or other hydrogen yielding substances.

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